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(54) Title: POLYMER PRODUCTS AND THEIR USES IN OIL (57) Abstract An invention relating to a copolymer comprising structural units derived from monomers which are (A) at least one ethylenically unsaturated alcohol, carboxylic acid or ester, with at least one of (B) an ethylenically unsaturated carboxylic ester with a polar group in the ester, and (C) an ethylenically unsaturated carboxylic amide, said copolymer being of molecular weight less than 20000.		

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POLYMER PRODUCTS AND THEIR USES IN OIL

The present invention relates to polymers, especially ester polymers, and for their preparation and use, particularly in diesel fuels.

Middle distillate oils e.g. diesel oils are complex mixtures comprising hydrocarbons of varying types and molecular weights among which are paraffins which are linear, branched chain or cyclic hydrocarbons having at least 18 carbons which can form waxy solids. These can separate at low temperature e.g. during winter and block fuel lines and filters.

We have discovered how to reduce the tendency to deposit wax from middle distillate oils e.g. diesel oils.

Carboxylic polymers have now been discovered which can act to reduce wax deposition.

The present invention provides a copolymer (including ter and higher polymers having structural units derived from monomers which are (A) at least one ethylenically unsaturated alcohol, carboxylic acid or ester, with at least one of (B) an ethylenically unsaturated carboxylic ester with a polar group in the ester, and (C) an ethylenically unsaturated carboxylic amide, said copolymers being preferably of molecular weight less than 20000. The copolymers may be derived from monomers A and/or B which are ethylenically unsaturated carboxylic acids or esters thereof, or esters of ethylenically unsaturated alcohols. The copolymers, may be acid esters, acid amides, mixed esters, ester amides or acid ester amides, or alcohol esters.

The present invention also provides a method of preparing the copolymers of the invention which comprises copolymerising the monomer A, with B and/or C, in particular, when monomer A is an ester, and especially when each of the monomers is

derived from an ethylenically unsaturated carboxylic acid or ester or amide, or each is derived from an ester of ethylenically unsaturated alcohol.

5 The present invention also provides a method of preparing the copolymers of the invention which comprises reacting an ester polymer having structural units of A which is an ester of an ethylenically unsaturated carboxylic acid (A^1), especially consisting essentially of such A^1 units, with an hydroxy compound containing at least one additional polar group and/or with an organic primary or secondary amino compound with or without at least one additional polar group. The present invention also provides a method of preparing the copolymers of the invention with structural units A, and B or C
10 in which structural units A^1 comprise carboxylic acids and optionally ester units, which comprises breaking an ester link in A^1 e.g. by hydrolysing a corresponding copolymer of the invention in which structural units A^1 are carboxylic esters especially ones without a polar side chain and especially of less than 6 carbon atoms in the alcohol part of the ester.

15 The present invention provides a method of preparing copolymers of the invention, which comprises reacting a polymer having structural units of A^{11} , which is at least one of an ethylenically unsaturated alcohol, an ester thereof and a mixture of ester units and units from said unsaturated alcohol A^{11} (but especially consisting essentially of such A^{11} units), with a carboxylic acid (or derivative thereof especially an ester)
20 containing at least one additional polar group.

The invention also provides complexes of the copolymers of the invention in which A is an ester monomer, and B and/or C contains a basic nitrogen atom (hereafter copolymers D), with at least one acid in particular a carboxylic acid, which may be polymeric or of molecular weight less than 1000 e.g. less than 400. There are also
25 provided complexes of the copolymers of the invention with structural units A^1 from carboxylic acid units alone or with ester units (copolymers E) with bases especially nitrogenous bases, which may be polymeric or of molecular weight less than 1000 e.g. less than 400. Preferably the complexes comprise the copolymers D and E.

The invention also provides a soluble concentrate with at least 10% at least 20%
30 by weight of a copolymer or complex of the invention, in a solvent especially an organic solvent for oil soluble copolymer and complexes. The copolymer or complex thereof may also be in a dispersion, with at least 10% e.g. at least 20% by weight of said

copolymer or complex, the dispersion being in a liquid medium in which the copolymer is insoluble or incompletely soluble. For oil soluble copolymers or complexes the medium is preferably aqueous while for water soluble ones the medium is preferably organic e.g. a hydrocarbon as described above.

5 The present invention also provides a middle distillate oil which comprises at least one copolymer or complex of the invention.

 The present invention also provides a method of reducing wax formation and/or deposition in a wax containing middle distillate oil which comprises mixing with said oil at least one copolymer or complex of the invention or concentrate or dispersion thereof,
10 in particular an oil soluble one and especially one containing a copolymer of an ester A or a complex thereof.

 In the copolymers are structural units from at least one monomer A¹ which is preferably an ethylenically unsaturated acid or ester thereof or mixture of both.

 The ethylenic unsaturated carboxylic acid for use, which may be monomer A¹,
15 may contain the unsaturated group alpha, beta or gamma, or in another location, to the carboxylic group. It may contain 3-6 carbon atoms, and is especially an aliphatic alpha ethylenically unsaturated carboxylic acid of formula R¹CH=CR²CO₂H, wherein each of R¹ and R² which may be the same or different is hydrogen or an alkyl group e.g. of 1-3 carbons, such as methyl, ethyl or propyl. Methacrylic and especially acrylic acids are
20 preferred. The acid may be a mono, di or tricarboxylic acid, examples of the diacid being fumaric, maleic and crotonic acids.

 The esters thereof for use as monomer A¹ may be from an aliphatic hydrocarbyl alcohol, with a short chain aliphatic group e.g. of 1-3 carbons and/or from a hydroxylic compound with a larger organic hydrocarbyl group such as of 4-24 e.g. 4-16 or 8-14
25 carbons.

 In the ester each of the aliphatic and/or organic hydrocarbyl groups may be saturated or unsaturated, e.g. all saturated or all unsaturated, but preferably at least one e.g. the short chain one is saturated and the rest saturated or unsaturated.

 The larger organic alcohol for use in the ester polymers may be aliphatic and
30 preferably linear, but may be branched (e.g. with a branch methyl group). The alcohol may be saturated i.e. an alkanol in which case preferably at least 20% or 40% of the saturated aliphatic groups have 4-20 e.g. 8-14 carbons. The alcohol may contain at least

one unsaturated group e.g. 1-4 such as 1 or 2 or 3 or 4, especially 1 unsaturated group. The aliphatic alcohol usually contains 4-24 or 6-20 carbons such as 8-18 carbons, especially 8, 10, 12 or 14 carbons. The alcohol may be natural or synthetic e.g. from oxo or ALFOL processes. Examples of suitable alcohols are with an alkyl group such as

5 hexyl, octyl, isooctyl, 2-ethylhexyl, decyl, dodecyl, lauryl, tetradecyl or myristyl group palmityl stearyl. The larger organic hydrocarbyl group may be a cycloalkyl group e.g. of 5-7 carbon atoms such as cyclo-hexyl or cycloheptyl, cyclopentyl or an aromatic group of 6-12 carbons, such a phenyl, tolyl or xylyl, or aralkyl group e.g. of 7-13 carbons such as benzyl or 2-phenyl ethyl. The alcohols especially aliphatic ones saturated or

10 unsaturated may be substantially pure, but are preferably mixtures of alcohols, e.g. of 10-14 carbons as with natural lauryl alcohol.

Preferably the monomer A is an ester of an aliphatic hydrocarbyl alcohol with a short chain aliphatic group of 1-5 carbon atoms, and an ethylenically unsaturated acid of 3-6 carbon atoms. Especially preferred are acrylates and methacrylates of methanol,

15 ethanol or tert butanol.

Thus monomer A may be of formula $R^1CH=CR^2CO_2R^3$, wherein each of R^1 , and R^2 which may be the same or different represents hydrogen or an aliphatic hydrocarbyl group e.g. an alkyl group of e.g. of 1-4 carbons such as methyl or ethyl and R^3 may be as defined for R^1 or R^2 or represents a hydrocarbyl group of at least 6 carbons such as an

20 alkyl or alkenyl group or other group e.g. as described for the larger hydrocarbyl group in the hydroxylic compound above. Preferably R^1 is hydrogen and R^2 is hydrogen alkenyl or alkyl, especially hydrogen or methyl and R^3 is hydrogen, alkyl or alkenyl, cycloalkyl, aryl or aralkyl. In Monomer A R^3 can consist essentially of hydrogen or hydrocarbyl or comprises a mixture of monomers A^1 , in which R^3 as hydrogen and R^3 as

25 hydrocarbyl may be present, the ratio being 0.5-99.5:99.5-0.5, such as 0.5-50:99.5-50 or 99.5-50:0.5-50, e.g. 10-40:90-60 or 90-60:10-40.

A mixture of structural units for monomers A^1 may be present with R^3 hydrocarbyl, in particular ones with short chain alkyl for R^3 and larger hydrocarbyl e.g. longer chain alkyl for R^3 (e.g. so the longer chain aliphatic alcohol described above is of

30 formula R^3OH). The molar ratio of monomers with such short to long chain group may be 0.5-99.5:99.5-0.5, in particular 10-90:90-10 especially 10-40:90-60. Increasing ratios of the longer chain monomer units tend to increase the hydrocarbon solubility of the

copolymers, as well as their molecular weight. The molar ratio of monomers with R³ as short chain to R³ as larger e.g. long chain may be 0.1-5:1:0.1-5 in particular 0.1-1:1:1-5, especially for oil soluble polymers and 1-5:1:0.1-1 for water soluble ones.

5 The transesterification product may contain mixtures of polymers so that the average carbon chain length of the medium length chain aliphatic groups is 4-13.9, 6-13.9 or 8.5 - 13.9 preferably 9-13.5 particularly 8 to 10 or 10-12 or 9-11 or 11-13 or 12-13.9 (in particular for diesel oils of Cloud Pt 0-20°C and/or pour point -40 to 0°C e.g. -20 to -10°C). Pour points were measured as defined in ASTM D97. If the short chain groups are also considered the overall average carbon chain of the aliphatic side chains is
10 preferably 4-10.9 e.g. 5-10.9 or 6-10.5 especially 6-8.5 or 8.5-10.8 particularly for middle distillate oils of Cloud Pt -20-+20°C e.g. 0 to +15°C and pour point -40 to -20°C.

Preferred monomers A¹ are acrylates of decyl and dodecyl alcohol, especially with at least 80% of 10 and/or 12 carbon alcohols respectively and at most 10% molar of any alcohol with 2 or 4 carbons higher or lower than 10 or 12 respectively.

15 Preferred copolymers A¹ are those with structural units from the above acrylates and structural units from at least one acrylate of an alcohol of 1-6 carbons, such as methanol or ethanol. The preferred copolymer units A¹ contain 30-90% or 40-90% preferably 50-90% molar of units from alcohols of 8-14 e.g. 9-13 carbons and 10-70% or 10-60% or preferably 10-50% molar of units from the alcohol of 1-6 carbons. Of
20 these 8-14 e.g. 9-13 carbon alcohols, at least 80% are preferably of 1 or 2 particular carbon number especially 8, 10 or 12.

Other preferred monomers A¹ are the vinyl esters of octanoic, decanoic and dodecanoic eg lauric acids, especially with at least 80% of 10 and/or 12 carbon acids and at most 10% molar of any alkanolic acid with 2 or 4 carbons higher or lower than 10 or
25 12 respectively.

Other preferred copolymers units A¹ are those with structural units from the above vinyl esters and structural units from at least one vinyl ester of an acid of 1-6 especially 2-6 carbons, such as acetic. The preferred copolymer units A¹ contain 30-90%, 40-90% or preferably 50-90% molar of units from alkanolic acids of 8-14 eg 10 or
30 12 carbons and 10-70%, 10-60% or preferably 10-50% molar of units from the acid of 1-6 e.g. 2-6 carbons. Of these 8-14 carbon acids, at least 80% are preferably of 1 or 2 particular carbon numbers, especially 8, 10 or 12.

Monomers A with groups R^3 as an aliphatic group of 14 or more e.g. 8 or more carbons may be substantially absent, or may be present so long as less than 30% e.g. 5-25% (or 5-15%) of the total aliphatic groups for R^3 in the monomers A have 6-35 or 12-35 or 15-35 carbons or may be present with an average total aliphatic side chain for R^3 of less than 12 carbons e.g. 1-11.9 such as 1-3.5, 1-2.5 or 4-8.

In the copolymers may also be structural units from at least one monomer B, which is an ester of an ethylenically unsaturated carboxylic acid and an organic monohydroxy compound with at least one additional polar group (B^1). The acid may be as described with respect to monomer A. The additional polar group may contain an oxygen, nitrogen or sulphur atom, especially one or more O and/or N atoms. The or each polar group may be a side chain substituent on a chain of carbon atoms or may interrupt a chain of carbon atoms. Examples of side chain substituents are ether groups e.g. of formula OR^5 and thioether groups of formula SR^5 , or corresponding sulfoxides or sulphones, or secondary amine groups e.g. of formula NR^5R^6 , wherein R^5 and R^6 are as defined below. Preferably the polar atom interrupts a chain of carbon atoms, so that the organic monohydroxy compound is preferably of formula HOR^4XR^5 , wherein X is O, S -SO, -SO₂ -or NR^6 , wherein R^4 represents a divalent organic group, in particular a hydrocarbyl group such as one of 1-16 carbons, as in an alkylene group e.g. of 1-4 carbons, a cycloalkylene group e.g. of 5-7 carbons, an arylene group e.g. of 6-12 carbons, or aralkylene or aryl bis alkylene group e.g. of 7-12 or 8-12 carbons respectively, each of R^5 and R^6 , which may be the same or different, represents an organic hydrocarbyl group e.g. of 1-14 carbons such as alkyl e.g. of 1-6 or 1-4 carbons, a cycloalkyl group of 5-7 carbons, an aryl group e.g. of 6-12 carbons or an aralkyl group of 7-12 carbons. Examples of R^4 are methylene, 1,2-ethylene (which are preferred) 1,3-propylene and 1,4-butylene or 1,4-cyclohexylene, or 1,2 or 1,3 or 1,4-phenylene, or 1,4-benzylene or 1,4-phenyl bis methylene (xylylene). Examples of R^5 and R^6 are methyl, ethyl, isopropyl or butyl, cyclohexyl, cyclopentyl phenyl, tolyl, xylyl or benzyl, but preferably methyl, ethyl or isopropyl in particular for R^6 and especially for both R^5 and R^6 . Thus preferably the $-R^4XR^5$ group in the monohydroxy compound is 2-methoxy ethyl and 2-methylthio ethyl, 2-ethylthio ethyl, 2,2-dimethyl amino-ethyl, and 2-p dimethylamino phenyl-ethyl.

The monohydroxy organic compound may also contain a hetero ring, preferably

- of 5, 6 or 7 ring atoms, and be of formula $\text{HO}(\text{R}^7)_a(\text{R}^8)_b\text{X}^1\text{R}^9$ wherein X^1 is O, S, SO or SO_2 or NR^{10} , and each of a and b, which may be the same or different, is 0 or 1, and R^7 is as defined above for R^4 , R^8 may be as defined for R^4 or, with R^9 may form a trivalent group, which with the oxygen S, SO or SO_2 or NR^{10} forms a heterocyclic group,
- 5 optionally with the ring carbon atoms interrupted with O and/or NR^{10} , R^9 forms the trivalent group above with R^8 or with R^{10} may form a divalent group which with the N atom to which they are bonded may form a heterocyclic group, optionally with the ring carbon atoms interrupted by O or NR^{10} (especially when R^{10} is as defined for R^6), and R^{10} may be as defined for R^6 or as defined above in a ring group with R^9 or may with R^8
- 10 or R^9 form an N heterocyclic ring group. Each of R^8 , R^9 and R^{10} when part of a ring can contain 1-5 carbons, subject to the ring containing 5-7 ring atoms.

Thus in the hetero ring containing compounds, when a is 1 and b is O, the R^7 group can be bonded directly onto the N atom of the ring formed with NR^9R^{10} as in N(2hydroxy methyl or 2 hydroxy ethyl) piperidine or N-(2hydroxy ethyl pyrrolidene)

- 15 When both a and b are O, the hydroxyl group can be bonded directly to the said ring N atom as in N-hydroxy piperidine. When a is O or 1 and b is 1, R^8 may form with R^9 and NR^{10} or the oxygen atom a hetero ring as in hydroxy N-methyl piperidine or hydroxy methyl tetra hydrofuran or hydroxy methyl pyridine (e.g. 2, 3 or 4-hydroxy methyl pyridine).
- 20 The ring heterocyclic ring formed with R^8R^9 and O or NR^{10} , or with R^9NR^{10} may be saturated or unsaturated, partly or fully (as in an N hetero aromatic ring) and may contain 1 nitrogen or oxygen atom and optionally 1 additional N and/or O atom. There may be 1 or more hetero rings e.g. 2 hetero ring fused or fused to each other, or 1 hetero ring and at least one carbocyclic ring, saturated or unsaturated fused or unfused to the
- 25 hetero ring. The ring groups can contain 3-12 carbons and 1-3 nitrogens. Examples of the rings are pyridine, piperidine, morpholine, tetrahydrofuran pyran rings, isoquinoline and quinoline.

- Examples of the organic monohydroxy compound with hetero-ring polar group are 2, 3 or 4 (2 hydroxy ethyl) tetrahydropyrrole or morpholine, 2, 3 or 4 hydroxyl N
- 30 methyl piperidine and 2 hydroxyethyl or hydroxymethyl substituted in a tetrahydropyran or tetrahydrofuran ring, especially with the substituent in a 2 position.

In the copolymers may also be structural units from at least one monomer C,

which is an ethylenically unsaturated carboxylic amide (C^1). The amide is derived from an ethylenically unsaturated carboxylic acid, which may be as described with respect to monomer A^1 , and ammonia or a primary or secondary amine. The amine may be of formula $HNR^{20}R^{21}$, where each of R^{20} and R^{21} , which may be the same or different
 5 represents an organic group or hydrogen, preferably one representing hydrogen, or R^{20} and R^{21} together with the N atom to which they are attached may form a heterocyclic ring.

Examples of the organic group are hydrocarbyl groups, such as are defined for R^5 or R^6 above, or hydrocarbyl groups containing at least one polar group, for which the
 10 nature and location of polar groups may be as described above in respect of monomer B^1 . Advantageously the amine containing the hydrocarbyl group and a polar group is of formula $H_2NR^{22}X^2R^{23}$, wherein X^2 is O, S or NR^{27} , R^{22} , R^{23} and R^{27} are as defined for R^4 , R^5 and R^6 respectively, or of formula $H_2N(R^{24})_c(R^{25})_dX^2R^{26}$, wherein c is 0 or 1, d is 0 or 1 X^2 is O, S or NR^{10} and R^{24} , R^{25} and R^{26} are as respectively defined for R^7 , R^8 and R^9
 15 above.

Thus for amines for use in monomer C^1 , which are hydrocarbyl amines R^{20} is preferably hydrogen while R^{21} is preferably a medium or short chain alkyl or alkenyl group, e.g. respectively of 4-24 e.g. 4-16, or 1-13 e.g. 1-3 carbons e.g. methyl or ethyl. R^{21} is preferably a medium chain length group of 6-18 carbons, in particular dodecyl, 2-
 20 ethyl hexyl or otherwise as defined for R^3 above. Examples of such amines are ethylamine, octylamine and dodecylamine. Benzylamine may also be used.

For amines in which R^{20} and R^{21} together with the N atom to which they are attached form a heterocyclic ring, the ring usually contains 5, 6 or 7, especially 6 ring atoms, with 1 nitrogen atom. The ring may be saturated or partly ethylenically
 25 unsaturated and may be unsubstituted or substituted by one or more alkyl groups e.g. of 1-6 carbons, such as methyl or ethyl. Examples of such amines are piperidine and tetrahydropyrrole and their ring methyl derivatives.

Preferably the amine contains an additional polar group as described above. The additional polar group may be a N or O atom not bonded in a ring or part of a ring.
 30 Preferably the N atom is not part of a ring, so the amine is of formula $H_2NR^{22}NR^{23}R^6$, wherein R^{22} , R^{23} and R^6 are defined above; R^{22} is especially alkylene of 1-4 carbons e.g. methylene or 1,2-ethylene, while R^{23} and R^6 are especially alkyl of 1-6 carbons, such as

methyl ethyl or isopropyl. Thus the amine may be 2(dimethylamino)ethylamine or 2-(diethylamino)ethylamine. The amine may also contain an oxygen atom not in a ring such as one of formula $H_2NR^{22}OR^{23}$ wherein R^{22} and R^{23} are as defined above, in particular R^{22} being alkylene of 1-4 carbons e.g. methylene or 1,2 ethylene, and R^{23} being especially alkyl of 1-6 carbons such as methyl, ethyl or isopropyl. Examples of such amines are 2-butoxyethylamine and 2-ethoxyethylamine. The amine may also contain an oxygen atom in a ring e.g. be of formula $H_2N(R^{24})_c(R^{25})_dOR^{26}$, wherein R^{24} is as defined for R^7 , and is especially methylene or 1,2-ethylene, and R^{25} and R^{26} and the O atom form a heterocyclic ring in the way R^8 and R^9 and the oxygen atom above form such a ring.

- 10 Examples of such rings are tetrahydrofuran, and tetrahydropyran rings. Examples of such amines are 2-aminomethyl-tetrahydrofuran and -tetrahydropyran. N heterocyclic ring substituted alkyl amines may also be used, in particular the amino analogues of the alcohols with a hetero cyclic ring described above with the OH group replaced by an NH_2 group. Examples of these are aminomethyl- and 2 amino ethyl-pyridines and
- 15 piperidines and morpholines.

In the copolymers may be structural units A^{11} from at least one ester of an ethylenically unsaturated alcohol, and/or said alcohol itself, including mixtures of alcohol and ester units e.g. with 1-50% alcohol with 99-50% ester or 99-50% alcohol and 1-50% ester. The structural unit A^{11} may consist essentially of said alcohol or said ester or

20 both. The ethylenically unsaturated alcohol may contain the unsaturated group, alpha, beta or gamma to the alcohol group or in another location. It may contain 2-6 carbons, and is preferably allyl alcohol, methallyl alcohol, alpha methyl vinyl alcohol or especially "vinyl alcohol" ($CH_2=CHOH$), which can form structural units for the ester polymers.

The carboxylic acid for use in the structural units with such unsaturated alcohols

25 may be an alkanolic acid e.g. of 1-24 carbons, e.g. 1-18 carbons such as 1-5 carbons, especially for alkanolic acids such as formic acetic, propionic and butyric acids, 3-24 carbon alkenolic acid e.g. oleic acid or 6-16 carbon alkanolic acids, in particular ones which are linear or have at least one methyl or ethyl branch. The carboxylic acid may have a larger organic hydrocarbyl group, such as one of 4-20 e.g. 6-18 carbons, e.g. an

30 alkanolic acid of 6-16 carbons such as hexanoic, octanoic, 2 ethyl hexanoic, isooctanoic, decanoic, lauric, dodecanoic, myristic or palmitic, or a cycloalkanoic e.g. of 6-8 carbons such as cyclohexanoic acid, or aromatic hydrocarbyl carboxylic e.g. of 7-14 carbons such

as benzoic or toluic, or aralkanoic acid e.g. of 8-15 carbons such as 2-phenyl ethanoic acid. The acid may contain 4-16 carbons such as 8-14 carbons, especially 8, 10, 12, 14 carbons. The acid may be natural or synthetic e.g. derived from oxo or ALFOL process alcohols. Examples of suitable acids are n octanoic, n decanoic, n undecanoic,

- 5 n dodecanoic, n tridecanoic or n tetradecanoic. The saturated or unsaturated acids may be substantially pure, but are preferably mixtures of acids, natural fatty acid as in commercial lauric acid.

- Preferably the monomer A¹¹ is an ester of an unsaturated alcohol with 3-6 carbons and a saturated carboxylic acid of 2-5 or 6-18 carbons. Especially preferred are
10 esters of "vinyl alcohol" and acetic or propionic acids.

Thus monomer A¹¹ may be of formula



- wherein each of R³⁰ and R³¹, which may be the same or different may be as defined for R¹ or R², while R³² may be as defined for R³, especially where R³CO₂H represents the
15 carboxylic acid which is an alkanoic acid of 1-6 carbons or one with a larger organic hydrocarbyl group as described above or a mixture thereof in particular ones in which the molar ratio of short to larger e.g. long chain acid groups for R³ is as described above. Preferably R¹ and R² are hydrogen and R³ is alkyl e.g. 1-5 or 6-18 carbons. The monomer A¹¹ may also be of formula R³³OCR³⁰=CHR³¹, where R³³ is hydrogen or
20 R³²CO.

- A mixture of monomer units from unsaturated alcohols may be present, in particular when R³³ is hydrogen, and when R³³ is R³²CO, especially in molar ratios of 0.5-99.5 : 99.5-0.5, in particular 5-95:95-5 or 10-50 : 90 - 50 or 90-50 : 10-50 e.g. 10-40 : 90-60 or 90-60 : 10-40. Increasing the proportion of R³²CO groups increases the
25 hydrocarbon solubility and molecular weight of the polymer. Mixtures of units from alcohols with short and longer chain groups for R³³ may have the proportions for R³ as defined for R³ above. Preferred are polymers from structural units of "vinyl" alcohol and vinyl acetate, laurate, palmitate.

- In the copolymers from unsaturated alcohols for A¹¹, may also be structural units
30 from at least one monomer B¹¹ which is an ester of an ethylenically unsaturated alcohol and an organic mono carboxylic acid with at least one additional polar group. The alcohol may be as described with respect to monomer A¹¹. The additional polar group

may contain an oxygen, nitrogen or sulphur atom, especially one or more O and/or N atoms. The or each polar group may be a side chain substituent on a chain of carbon atoms or may interrupt a chain of carbon atoms. Examples of side chain substituents are other groups e.g. of formula RO^5 , or secondary amine groups e.g. of formula NR^5R^6 ,
5 wherein R^5 and R^6 are as defined above. Preferably the polar atom interrupts a chain of carbon atoms, so that the organic carboxylic acid is preferably of formula $HOOCR^4XR^5$, wherein X, R^4 , R^5 are as defined and exemplified above.

Preferably the $-R^4XR^5$ group in the carboxylic acid compound is methoxy phenyl, methoxy methyl, 2-methoxy ethyl and methylthio methyl, 2-methylthio ethyl or 3-
10 methylthio propyl, methylthio phenyl-, 2-phenylthio ethyl-, 2,2-dimethyl amino-ethyl, 2-dimethylamino phenyl-ethyl (especially with the dimethylamino group in o or p position, dimethylamino methyl and dimethyl amino phenyl.

The organic carboxylic acid may also contain a hetero ring, preferably of 5, 6 or 7 ring atoms, and be of formula $HOOC(R^7)_a(R^8)_bX^1R^9$ wherein R^7 , R^8 , R^9 , X^1 are as
15 defined and described above.

Thus in the hetero ring containing compounds, when a is 1 and b is O, the R^7 group can be bonded directly onto the N atom of the ring formed with NR^9R^{10} as in N(carboxy methyl) piperidine. When a is O or 1 and b is 1, R^8 may form with R^9 and NR^{10} or the oxygen atom a hetero ring as in N-methyl piperidine carboxylic acid or tetra
20 hydrofuran carboxylic acid or pyridine carboxylic acid or picolinic acid.

The ring heterocyclic ring formed with R^8R^9 and O or NR^{10} , or with N^9NR^{10} may be saturated or unsaturated, partly or fully (as in an N hetero aromatic ring) and may contain 1 nitrogen or oxygen atom and optionally 1 additional N and/or O atom. There may be 1 or more hetero rings e.g. 2 hetero ring fused or infused to each other, or 1
25 hetero ring and carbocyclic ring, saturated or unsaturated fused or unfused to the hetero ring. The ring groups can contain 3-12 carbons and 1-3 nitrogens. Examples of the rings are pyridine, piperidine, morpholine, tetrahydrofuran pyran rings, isoquinoline and quinoline.

Examples of the organic monocarboxy compound with hetero-ring polar group
30 are 2,3 or 4 (carboxymethyl) tetrahydropyrrole or morpholine, N methyl piperidine carboxylic acid and carboxymethyl or carboxy substituted in a tetra hydropyran or tetra hydrofuran ring, especially with the substituent in a 2 position.

The copolymer may have structural units from monomers A and B (including A^1B^1 or $A^{11}B^{11}$), in which case the molar percentages may be 30-95%B, e.g. 30-60% or 60-90% B (especially when B^1 is derived from a nitrogenous alcohol) or 60-80% (especially when B^1 is derived from an ether alcohol), with 70-5%A, e.g. 70-40%A or 40-10%A or 40-20%A; the copolymer especially consists essentially of structural units of such monomers. The copolymers may contain at least 10.1% by weight of structural units from B, e.g. 11-80 such as 35-60wt% in particular in copolymers of A and B, especially when monomers A^1 comprise both long and short chain aliphatic alcohol groups e.g. from R^3OH in particular ones with at least 30% of long chain groups, based on the total of said aliphatic groups. The copolymers may contain (a) 10-80% e.g. 10-70% or 20-50% or 50-80% of short chain monomer A units (including A^1, A^{11}) (e.g. alkyl(meth)acrylate or vinyl alkanoate esters with 1-4 carbons in the alkyl or alkanoate group), (b) 10-60% e.g. 20-40% or 10-30% of larger monomer A units (including A^1, A^{11}) (e.g. alkyl-(meth)acrylate or vinyl alkanoate esters with 4-18 e.g. 6-18, 6-12 or 4-8 carbons in the alkyl or alkanoate group) and (c) 5-50% e.g. 10-30% of structural units from monomer B (including $B^1 B^{11}$), in particular one in which the polar group is 1 or 2 amine or ether groups. The molar proportions of the units (a):(b):(c) are usually 0.5-4 (e.g. 0.5-3 or 2-3.5): 0.5-1.5 (e.g. 0.8-1.3 especially 1) : 0.5-1.5 (e.g. 0.8-1.3 especially 1 or 0.5-1.0). The copolymer may have structural units from monomers A and C including $A^1 C$ in which case the molar percentages may be 5-80%C e.g. 5-50% or 8-25 or 20-45%C and 95-20%A, e.g. 95-50%, or 92-75% or 80-55%A, the copolymer especially consisting essentially of structural units of such monomers. The copolymers may also contain units from monomers A, B and C (including $A^1, A^{11}, B^1, B^{11} C^1$) in which case the molar percentages may be 5-60%B, e.g. 20-50%B, 5-50%C e.g. 8-25%C, and a preferred total of B and C of 20-95% e.g. 40-80% or 50-70%, and a molar percentage of A of 5-80% e.g. 60-20% or 50-30%, the copolymer especially consisting essentially of structural units of such monomers). The units of monomer A may be from ester, acid or both acid and ester monomers and the above percentages apply to the amounts of ester monomer as sole A unit, or acid monomer as sole A unit or the total of both. Preferred are copolymers with an ester monomer units for A, and basic N containing monomers for B and/or C (i.e. copolymers D) or copolymers with a carboxylic acid units for A, and non basic N containing monomers B and/or C (i.e.

copolymers E), or carboxylic acid for A with basic N containing monomers for B and/or C which are zwitterions.

The copolymers may be made by direct copolymerisation of the monomer units, A, especially when it only contains ester groups and not carboxylic acid ones, and B and/or C, especially when the monomer is free of any NH group. In the direct copolymerization, the monomers are usually all present from the start, though partial or complete polymerization of some monomer(s) e.g. A, followed by addition of monomer e.g. B, and optionally A, as in graft polymerization may be performed. Preferably however, the polymers by direct polymerization are random not graft or block copolymers. Preferably monomers of type A^1 , B^1 and/or C^1 react together, or of type A^{11} and B^{11} , though ones of A^1 and B^{11} or A^{11} and B^1 can be reacted.

The copolymerisation may be performed in a conventional manner e.g. with or without a diluent e.g. a hydrocarbon solvent, such as hexane, heptane, or a higher boiling hydrocarbon oil, at a temperature of 25-120°C, such as 60-100°C, and optionally in the presence of a free radical catalyst, such as a peroxide (e.g. benzoyl peroxide) or azo catalyst such as azobis isobutyronitrile. The polymerisation is usually performed under inert conditions e.g. under nitrogen or argon. The polymerisation time may be 0.5-40hr, preferably 5-25hr at 60-100°C. At the end of the polymerisation, the reaction product may be purified by evaporation under vacuum to remove unreacted monomer, and/or precipitation of the product with methanol from a liquid aromatic or aliphatic hydrocarbon solution of the product.

Preferably however, the copolymers A + B are made by reaction of a polymer of one or more ester monomer units A (i.e. A^1 or A^{11}) which are derived from an unsaturated acid (or unsaturated alcohol), with an organic mono hydroxy compound (or organic carboxylic acid respectively) with at least one additional polar group, as described above, in particular one of formula HOR^4XR^5 or $HO(R^7)_a(R^8)_bXR^9$ (or $HO_2CR^4XR^5$ or $HO_2C(R^7)_a(R^8)_bX^1R^9$ respectively). Instead of either of the latter carboxylic acids a corresponding lower alkyl (C_{1-4}) ester (e.g. methyl, ethyl propyl tertbutyl ester may be used.

Preferably copolymers $A^1 + C^1$ derived from an unsaturated acid are made by reaction of a polymer of one or more corresponding ester monomer units A^1 , with ammonia, or a primary or secondary amine, in particular one of formula $HNR^{20}R^{21}$ or



- The reaction may be performed in the absence of but preferably in the presence of a liquid aromatic or aliphatic hydrocarbon solvent, by reaction of an ester hydroxyl, acid, acid ester or hydroxy ester polymer from monomer A, especially an ester with 1-4
- 5 carbons in the alcohol (or acid) group with the organic monohydroxy compound (or carboxylic acid) having the polar group, or ammonia or said amine in the case of unsaturated acid polymers. The reaction may be performed with an amount of the said compound or ammonia or amine substantially corresponding to the amount needed for the degree of conversion required, or an amount in excess of this e.g. substantially
- 10 corresponding to an equimolar amount (based on the units of monomer ester A in the starting polymer) may be used and the reaction stopped when the desired degree of reaction has occurred e.g. as found from the amount of distilled by product lower alcohol or carboxylic acid or ester thereof e.g. methyl acetate. The reaction may be performed at 50-180°C e.g. 60-120°C or 100-160°C for 1-30 e.g. 5-20 hours, in the absence or
- 15 presence of a catalyst e.g. an organic soluble strong acid such as an aromatic sulphonic acid e.g. p-toluene sulphonic acid or a basic catalyst, such as an alkali metal alkoxide e.g. sodium methoxide or ethoxide (added as such or prepared in situ from alkali metal and by product lower alkanol) or a polyvalent metal alkoxide such as tetra methyl, tetra ethyl or tetraisopropyl titanate. Amounts of the catalyst e.g. basic ones such as alkali metal
- 20 alkoxide may be 0.05-5% e.g. 0.1-1% by weight of the feed polymer. Basic catalysts are preferred for the reaction of the polymer esters derived from the unsaturated acids, while acid catalysts are preferred for the reaction of the polymeric esters derived from unsaturated alcohols. During the reaction the by product lower alcohol or lower alkyl carboxylate is preferably evaporated. At the end, any solvent is advantageously
- 25 evaporated, while optionally unreacted polar mono hydroxy compound or acid or amine may be evaporated e.g. under reduced pressure. The reaction which is transesterification may be performed substantially to completion e.g. 90-100% especially 95%-100%, with substantially no unreacted starting polymer e.g. 0-10% especially 0-5%, but advantageously the amount of reaction is 30-90% e.g. 55-75% or 70-90%.
- 30 In the transesterification the ester polymer which can be reacted with the hydroxy compound with the polar group may comprise only short chain alkyl(meth) acrylate monomer units or larger alkyl(meth) acrylate polymer units or both larger and short chain

units. The last copolymers may themselves have been made by copolymerization or transesterification from the short chain alkyl polymers and larger alcohols e.g. long chain alcohols according to the general procedure described above. In a similar way the ester polymer to be reacted with the organic carboxylic acid (or ester) may comprise short chain alkanoate side chains, or larger organic carboxylate side chains or both. The latter may be made from the corresponding short chain alkanoate polymers and reaction with the larger acids.

The reaction of ester polymers with the amines may be performed in a similar manner to that of the polar alcohols, but in this case the reaction may be performed to the extent as described for the transesterification above but in particular 30-90% e.g. 50-80%; however preferably the reaction may be performed to 5-90% reaction, such as 5-50% such as 10-40% e.g. 10-20% or 30-50%.

Copolymers of A and B and/or C, in which the structural units from monomer A contains free carboxylic groups as sole monomer A units or mixed with ester units or free hydroxyl groups may be made by cleavage of the ester link in A, e.g. by hydrolysis or hydrogenolysis (e.g. for benzyl esters) of the corresponding copolymer in which A is an ester monomer. The hydrolysis, which is usually performed in solution in an organic solvent, may be acid or base catalysed e.g. with an alkane or aromatic sulphonic acid, e.g. methane sulphonic or toluene sulphonic acid or a base such as sodium or potassium hydroxide, especially with distillation of by product alcohol from the ester. Weight amounts of the catalyst may be 0.1-5% by weight or preferably 1-10 equivalents per carboxylic ester group in monomer A in the copolymer. When carboxylic acid groups are required copolymers with ester monomers A based on lower alkyl or lower alkanoate esters are preferred as starting materials. The product free acids or acid esters may be isolated if desired by extraction into aqueous base, e.g. sodium hydroxide solution which can be separated from unreacted ester copolymers A+B and then the free acids or acid esters recovered by filtration or extraction after acidification of the aqueous solution. The product from alcohols e.g. polyvinyl alcohol derivatives may be isolated by extraction. The copolymers with free hydroxyl and/or carboxyl are of particular value for forming complexes (see below).

The nitrogen containing polar group in the copolymers may be present in the form of a primary, secondary or tertiary amine or a quaternary salt. Quaternisation may

be performed by reacting a copolymer of the invention having basic nitrogen atoms with a quaternising agent e.g. an organic halide e.g. chloride or organic sulphate, in either of which the organic group is an alkyl group e.g. of 1-20 carbons such as methyl, ethyl, dodecyl, stearyl, alkenyl group of 3-20 carbons e.g. 3-6 such as allyl, cycloalkyl e.g. of 5-7 carbons such as cyclohexyl, aralkyl e.g. a hydrocarbyl group of 7-30 carbons such as benzyl, 2-phenyl ethyl or dodecyl benzyl. Thus a copolymer (derived from an unsaturated acid or alcohol) having ester groups from a polar amino alcohol (or amino acid) e.g. structural units from 2 dimethyl amino ethyl acrylate (or (pyridine methyl)acrylate) and e.g. methyl acrylate (and optionally larger organic acrylates) or units from vinyl 2-dimethyl (amino propionates) and e.g. vinyl acetate (and optionally a vinyl larger alkanooate., may be reacted with dimethyl or diethyl sulphate or benzylchloride, preferably with the desired proportion of quaternisation agent to basic nitrogen and in a hydrocarbon solvent. The amount of quaternisation may be such as to provide 1-20% molar of structural units with a quaternary group, e.g. 5-10%; there may also be present 0-20% molar of structural units with a basic nitrogen atom i.e. unquaternised, preferably when the total of basic nitrogen and quaternised nitrogen is 5-20%. Thus the degree of quaternisation may be partial or substantially complete. At the end of the quaternisation, any excess of quaternisation agent may be separated e.g. by evaporation, and the polymer product, if desired, isolated.

The copolymers of the invention may be crystalline but are preferably noncrystalline e.g. amorphous. The ester copolymers of the invention are usually oil soluble e.g. dissolves to an extent of at least 50ppm e.g. at least 200ppm in kerosene at 25°C. The acid or alcohol copolymers of the invention are usually water soluble e.g. to an extent at 25°C of at least 50ppm e.g. at least 200ppm at at least one pH in the range 1-14, especially 2-7 or 8-13, in particular to at least 1%.

The invention also provides complexes or salts of the copolymer D, having a Lewis base in the side chain, especially ones which are nitrogenous, with an acid which is preferably a carboxylic acid or sulphonic acid. The carboxylic acid may be an organic mono, di or tri carboxylic acid, in particular one of 1- 24 carbons, e.g. an alkanolic or alkenolic acid of 1-16 carbons e.g. 2-6 or 6-14 carbons such as formic, acetic, propionic, 2-ethylhexanoic, lauric, oleic or stearic acid. Examples of the sulphonic acid are alkyl and aryl sulphonic acid, e.g. alkylsulphonic acids of 1-10 carbons such as 1-6 carbons

such as methane and propane sulphonic acids, or aromatic hydrocarbyl sulphonic acids e.g. of 6-24 carbon atoms such as benzene, toluene, xylene or dodecylbenzene sulphonic acids. The molar proportion of Lewis base e.g. basic nitrogen atoms or O or S atoms in ether groups in the copolymer e.g. in amino groups to acid groups, in the carboxylic or sulphonic acid may be 10-0.1:1 e.g. 4-0.5:1.

The above examples are of acids of molecular weight less than 1000 e.g. less than 400. But in addition polymeric acids may be used e.g. polymers with a plurality of carboxylic and/or sulphonic acid groups and optionally a Molecular weight of 400-20,000 e.g. 800-10,000 or 1500-5000. Such polymers usually have a hydrocarbon backbone and pendant acid groups, and are made by polymerisation of ethylenically unsaturated acid monomers e.g. (meth)acrylic acids. or vinyl and methyl vinyl sulphonic acids. Other polymeric carboxylic acids are polymeric carboxylic acid esters, e.g. made by copolymerising the corresponding monomers e.g. acrylic acid and alkyl acrylates, but preferably as polymeric carboxylic acid esters or acids by at least partial e.g. complete hydrolysis of copolymers of monomer A with the group R^3 in the aliphatic alcohol a mixture of long and short chains, as described above. Such latter copolymers may be made by transesterification of the short chain ester polymers from A with long chain alcohol. The molecular ratio of basic N, O or S atoms in the copolymer of the invention to acid group in the polymeric acid may be 0.1-10:1 e.g. 0.5-2:1.

The invention also provides complexes or salts of copolymer E, which contain carboxylic acid groups with a base which may be inorganic or organic. Examples of inorganic bases are oxides, hydroxides, carbonates and bicarbonates of ammonia, alkali metals and alkaline earth metals, e.g. of sodium, potassium calcium or magnesium, especially sodium and potassium salts of the copolymer E. Examples of the organic bases are amines, in particular primary, secondary or tertiary amines, such as those of formula $HNR^{20}R^{21}$ as defined above or polyamines, such as ethylene diamine, diethylene triamine and higher homologues, or hexamethylene tetramine. The above organic bases usually have a molecular weight below 1000 or below 400, but polymeric amines may also be used with molecular weights above this e.g. 400-20000 such as 800-10000 or 1500-5000. Examples of such polymeric amines are polyethylene imine and polypropylene imine. The base may also be a Lewis base, in particular an oxygen or sulphur containing compound, especially with at least one oxygen atom in an ether (or

thioether) or hydroxyl (or thiol) group. Thus the base may be of molecular weight less than 1000, e.g. less than 400, or may be polymeric with molecular weight above 1000.

Examples of the bases of molecular weight less than 1000 are aliphatic mono ols (or thiols), di, tri or tetra polyols (or polythiols), such as lower alkanols e.g. methanol or ethanol, or alkylene glycols, e.g. ethylene or propylene glycols, or glycerol or pentaerythritol, or glycol ethers such as alkylene glycol ethers, e.g. mono or di lower alkyl ethers of mono, di or poly alkylene glycols. Polymeric bases may also be polyalkylene glycols or ethers thereof e.g. polyethylene glycol or block or random

copolymers of ethylene and propylene glycols. Other examples of polymeric bases are partially hydrolysed polyvinylacetate. The molar ratio of acidic groups in the copolymer of the invention to basic group or atoms in the base e.g. basic N, O or S atoms may be 0.1-10:1 such as 0.5-2:1. The complexes may be made by mixing the basic copolymer and carboxylic acid (or acid copolymer and base) in the desired proportions and preferably in a solution in an organic solvent such as an aromatic hydrocarbon such as benzene, toluene or a xylene followed optionally by evaporation or other isolation method, preferably under vacuum and reduced temperature e.g. less than 100°C minimize any reactions other than complex formation.

Preferably the base copolymer D forms a complex with acid copolymer E the molar ratio of base to acid groups being 0.1-10:1 e.g. 0.5-2:1.

The monomer A¹¹ may also be derived from an ester of an ethylenically unsaturated alcohol with a carboxylic acid, and in this case the monomer B¹¹ is usually derived from the ester of an ethylenically unsaturated alcohol and carboxylic acid with at least one extra polar group. Such copolymers of A¹¹ and B¹¹ are obtained by or are obtainable by reaction e.g. transesterification of the ester of the unsaturated alcohol with the polar carboxyl i.e. acid or an ester (or acid halide) thereof. The reaction may be performed to at least 30% e.g. 30-90% completion.

The present invention also provides blends of one or more of the copolymers of the invention, e.g. solely of different polymers of the same type e.g. ester A+B or ester A+C polymers or acid A+B or acid A+C polymers, the differences lying in different molecular weights, different chain lengths for the ester or nature of the polar group in B or nature of the amide in C. Blends may contain 90-10:10-90 e.g. 30-70:70-30 proportions of the 2 copolymers.

The ester complexes of the invention are usually oil soluble e.g. dissolve in kerosene at 25°C to at least 50ppm such as at least 200ppm, while the acid or alcohol complexes are usually water soluble e.g. to an extent at 25°C of at least 50ppm e.g. at least 200ppm at at least one pH in the range 1-14, especially 2-7 or 8-13, in particular to at least 1%.

The present invention also provides a soluble concentrate of at least 10% by weight of a copolymer or complex of the invention, e.g. 10-40% such as 20-30% by weight in a solvent e.g. water (for water soluble copolymers or complexes) or an organic solvent, such as an aromatic hydrocarbon e.g. toluene or xylene or a mixture of methyl benzenes or kerosene for oil soluble copolymers or complexes. If desired the solvent may be a mixture e.g. of the aromatic hydrocarbon and a polar oxygenated solvent such as methanol ethanol or isopropanol. The copolymer of complexes may be made as such in the above solvent, which may be concentrated if required, but preferably they are made in a solvent, the solvent evaporated and/or the copolymer or complex isolated if desired and the above concentrate made with the specifically desired solvent (or especially solvent mixture). A concentrate is often easier to handle for the proposed uses than pure product or a dilute solution.

However, in some cases the copolymer or complex may not dissolve in the desired organic solvent to the desired extent for a concentrate, so in these cases a dispersion in an organic solvent e.g. an aromatic hydrocarbon (as above) may be made. When the copolymer or complex does not dissolve in water, a dispersion in water of the copolymer or complex may be made e.g. with at least 5% such as 5-40 or 10-30% by weight of the copolymer or complex. The dispersion may contain water as continuous medium and the copolymer or complex as such or in a solution in organic solvent (e.g. an aromatic hydrocarbon as above) as the disperse phase. A polar organic solvent e.g. as described above may also be present. The dispersion preferably also contains a surfactant to stabilise it (e.g. in amount 0.1-5% by weight) especially one compatible with the overall nature of the copolymer, e.g. basic polymers preferably have nonionic or cationic surfactants, while acid polymers preferably have nonionic or anionic surfactants.

The polymers of the present invention may have a molecular weight of less than 20,000 such as 1000-19999, 1000-19000 such as 1500-15000 especially 2000-7000 or 7000-13000 (Mw, weight average molecular weight) and the molecular weight

distribution (M_w/M_n) may be 1.2-20 e.g. 1.2-10, preferably, 1.4-2 or 2-20 e.g. 5-15. As used herein, unless otherwise specified, the term "Molecular Weight" of an ester or amide polymer produced by reaction of the corresponding precursor ester polymer and alcohol, ammonia or amine means the weight average molecular weight of the ester polymer obtained by calculation from the percentage conversion (based on spectroscopic analysis) and the molecular weight of the precursor ester or amide polymer, or the weight average molecular weight of the ester or amide polymer itself, the molecular weight being determined by gel permeation chromatography (GPC) against polystyrene standards as described in the Aldrich Chemical Company's Standard Test Method for GPC. The term Molecular weight of an acid polymer made from ester polymer e.g. by hydrolysis is likewise defined. The term "Molecular Weight" of an ester or amide polymer produced by direct polymerisation of the corresponding ester or amide means the weight average molecular weight of the ester or amide polymer determined by gel permeation chromatography (GPC) against polystyrene standards as described in the Aldrich Chemical Company's Standard Test Method for GPC. The term molecular weight of an acid polymer made by direct copolymerization is likewise defined.

The copolymers or complexes, whether in solution, concentrate, or dispersion form or otherwise, may be used to alleviate problems with wax deposition in middle distillate oils.

The oil whose flow characteristics are to be improved usually comprise a liquid hydrocarbon, which is a middle distillate oil.

The middle distillate oil is a petroleum based oil obtainable from crude oil, as a fraction distilling in the lighter, e.g. kerosene or jet fuel range to the heavy fuel oil range. Middle distillates may comprise atmospheric or vacuum distillate, cracked gas oil or a blend of straight run and thermally and/or catalytically cracked distillate. Examples include, kerosene, jet fuel, diesel fuel, heating oil, visbroken gas oil, light cycle oil, vacuum gas oil, light fuel oil and fuel oil. The boiling range or the middle distillate measured (according to ASTM D86) is usually 100-500°C e.g. 140-400°C. Diesel oil e.g. for vehicles which may be for summer or especially winter use, is preferred. Oil or water soluble copolymers or complexes or organic or water concentrates or dispersions may be mixed with one phase distillate oils. If desired the oil may be in the form of a water in oil emulsion especially with 5-30% wt water, in which case preferably oil

soluble, but water insoluble, copolymers or complexes are used. The middle distillate oil is usually for use as a fuel so the invention also comprises use of copolymers, complexes or dispersions of the invention as wax formation or wax deposition inhibitors in a middle distillate fuel oil, prior to burning. Also provided is a method of burning a fuel oil which
5 comprises burning a middle distillate fuel oil comprising at least one copolymer, complex or dispersion of the invention.

The fuel oil may also contain at least one additive, e.g. (a) flow improver such as a polyoxyalkylene compound e.g. a polyoxyethylene diester, diether or ester/ether or mixture thereof, or ethylene vinyl acetate copolymer, or nitrogenous compound with at
10 least one long chain such as of 8-40 carbons, hydrocarbyl bonded directly to nitrogen such as an amine salt or amide, (b) detergent, (c) anti foam, (d) ignition improver, (e) lubricity additive or (f) corrosion inhibitor. The present invention also provides a concentrate in a liquid solvent e.g. hydrocarbon oil comprising at least one is Polymer of the invention and at least one of said additives (a)-(f), each of the said Polymer and
15 additive(s) being present in an amount in the concentrate of at least 1% e.g. at least 5% (by weight). Weighting agents for oil based drilling e.g. insoluble ones such as barite haematite or galena are usually substantially absent.

The hydrocarbon may be primarily aliphatic or aromatic in nature, but may be mixtures of aliphatic and aromatic hydrocarbons. The hydrocarbon may contain up to 5%
20 by weight of wax. The hydrocarbons may in the absence of the copolymers of the invention, have a cloud point value of at least -20°C e.g. -20 to 0°C such as -15 to -5°C ; pour point of such hydrocarbons may be $1-20^{\circ}\text{C}$ e.g. $1-10^{\circ}\text{C}$ lower than the WAT value and may be -30°C to 0°C e.g. -20°C to -5°C . The polymers of the invention may reduce the pour point value of the liquid hydrocarbon by at least 3°C e.g. $3-21^{\circ}\text{C}$ such as $6-15^{\circ}\text{C}$,
25 and can reduce the rate of wax deposition per unit time.

The copolymers may also delay the onset of wax nucleation in the oil as shown by light scattering and they may also reduce the pour point and/or modify the wax crystals or disperse the wax. In particular the copolymers may reduce the weight of wax deposition either by reducing the rate of deposition and/or by reducing the temperature
30 of onset of deposition. The reduced wax deposition may be associated with reduced wax in suspension (i.e. reduced total wax formation) or the same or an increased amount of wax in suspension (i.e. the altering distribution of wax between suspension and

deposition).

The polymers concentrates or dispersions may be mixed in a portion with the hydrocarbon to be protected or may be mixed batchwise, continually or continuously with a body of the hydrocarbon e.g. oil usually moving liquid body, preferably added to a line containing flowing hydrocarbon to be protected, upstream of a cooler location where wax deposition may occur in the absence of said compound e.g. one below the Wax Appearance or Cloud Point temperature of the oil. If desired the polymers concentrates or dispersions may be added to a tank of the oil e.g. to inhibit deposition of wax. The amount of polymer, whether as such or in concentrate or dispersion, added may be 10-10,000 ppm e.g. 20-5000 or 50-1000 ppm based on the weight of oil e.g. hydrocarbon. The polymer preferably dissolves in said oil to an extent of at least 10ppm e.g. at least 100ppm such as 100-5000ppm.

Example 1

Preparation of copolymer of methylacrylate and 2-(hydroxymethyl)pyridine.

A solution of poly(methyl acrylate) in toluene (41.5% in toluene, polymer average molecular wt. 6,000)[4.34g, 50.5mmol] was dissolved in toluene [50ml]. 2-(Hydroxymethyl)pyridine [4.40ml, 45.6mmole] was added and the solution heated to 60°C. Sodium methoxide in methanol (25% solution) [740μL] was added in one portion and the solution brought to reflux under anhydrous conditions for 7.5h (bath temperature 150°C). At periodic intervals during the reflux the distillate was removed and replaced with fresh toluene [4 x 25 ml]. The reaction product was concentrated to dryness to afford the transesterified polymer (7.97g). The product contained (by NMR) 71% transesterified polymer, 16% unreacted polymer and 13% unreacted alcohol. Yield of transesterified product as a proportion of total polymer = 82% (by nmr) (i.e. 82% of the CO₂ CH₃ groups have been replaced by CO₂CH₂ pyridyl groups. The product had a calculated Molecular Weight of 10,400.

Examples 2, 3

In a similar manner to that of Ex.1 were made the corresponding transesterified products from 3-hydroxymethyl pyridine (87% reaction) and 1-(2-hydroxyethyl) pyrrolidene (71% reaction) with calculated Molecular Weights of 10,700 and 10,100 respectively.

Example 4

The process of Ex. 1 was repeated with 4.3g of the polymer, n-hexanol (1.25ml), 4-hydroxymethyl pyridine (1.09g) and Na OMe in methanol (250 μ L) and reaction in xylene (40ml) at reflux for 6.5hr. The reaction product after cooling was concentrated to dryness. The polymer product contained hexyl ester (20%) and 4-pyridylmethyl (16%) and unreacted methyl ester side chains (64%). The overall transesterification degree was 36%, and the calculated MW was 7700.

Example 5

The process of Ex. 4 was repeated with the 4-hydroxymethyl pyridine replaced by 2-dimethylaminoethanol (10ml) and reaction in toluene 40ml, not xylene. The polymer product contained hexyl ester (17%) 2-dimethylaminoethyl ester (20%) and unreacted methyl ester side chains (63%). The overall transesterification degree was 37%, and the calculated MW was 7500.

Example 6

The process of Ex. 4 was repeated with polymethylacrylate (7.94g MW 3000) hexanol (1.87g) 4-hydroxymethylpyridine (2.01g) and reaction in xylene 70ml at 160°C for 7.5hr. The polymer product contained hexyl ester and 4-pyridylmethyl and unreacted methyl ester side chains.

Example 7

The process of Ex. 6 was repeated with polymethyl acrylate (7.94g), n-hexanol (1.87g) and 2-dimethylamino ethanol (1.59g) and reaction in toluene (70ml) at 140°C for 7.5hr. The polymer product contained hexyl ester 2-dimethylaminoethyl ester and unreacted methyl ester side chains.

Example 8

The copolymers of Ex. 1-3 were each dissolved in toluene to 25% concentrates.

Example 9

The copolymer of Ex. 1 (3g) was dissolved in toluene 30ml and water (1ml) added. The mixture obtained was stirred for 48hr at room temperature and then the solvent evaporated under vacuum to leave a white solid, which nmr showed to contain carboxylic acid groups (from hydrolysis of the methyl ester in the copolymer) (about 6% of the total monomer units).

Example 10

Blends were made of the transesterification product of Ex. 1-9 and a middle distillate

fuel oil, which had the following characteristics. Density kg/m^3 at 15°C 838,1, Sulphur content 300ppm, Kinematic viscosity at 40°C 2.452 cSt, Cloud Pt -9°C CFPP (Cold Filter Plug Pt.) -9°C , SFPP (Simulated Filter Plug Pt.) -8°C , Pour Point (determined according to ASTM D97) -12°C , IBP (Initial Boiling Pt.) 154.1°C , boiling range (according to ASTM D86, 10% (vol.) recovered as 197.4°C , 50% at 268.3°C , 90% at 331.8°C , 95% at 348.6°C and Final Boiling Pt. 362.5°C . In this distillation 98.3% (vol.) was distilled, 1.3% was residue and 0.4% was lost. The cetane index of the fuel oil (according to IP 380) was 50.4.

Blends were made with 100ppm and 500ppm of the products of Ex.1-9 and the diesel fuel oil.

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Claims:

1. A copolymer comprising structural units derived from monomers which are (A) at least one ethylenically unsaturated alcohol, carboxylic acid or ester, with at least one of (B) an ethylenically unsaturated carboxylic ester with a polar group in the ester, and (C) an ethylenically unsaturated carboxylic amide, said copolymer being of molecular weight less than 20000.
2. A copolymer as claimed in claim 1, which is derived from monomers A and/or B which are ethylenically unsaturated carboxylic acids or esters thereof, or esters of ethylenically unsaturated alcohols.
3. A copolymer as claimed in claim 1 or claim 2, wherein monomer A is an ester monomer, and B and/or C contains a basic nitrogen atom.
4. A copolymer as claimed in claim 1 or claim 2 wherein monomer A is derived from ethylenically unsaturated carboxylic acids (A¹) alone, and/or wherein said copolymer comprises an ester.
5. A copolymer as claimed in any preceding claim wherein said polar group in monomer B contains an oxygen, nitrogen or sulphur atom.
6. A copolymer as claimed in any preceding claim, wherein C is an ethylenically unsaturated carboxylic amide derived from an ethylenically unsaturated carboxylic acid.
7. A copolymer as claimed in any preceding claim which is noncrystalline.
8. A copolymer as claimed in any preceding claim, which consists essentially of structural units derived from 70 - 5 molar % A and 30 - 95 molar % B.
9. A copolymer as claimed in any of claims 1 to 7, which consists essentially of units derived from 95 - 50 molar % A and 5 - 50 molar % C.

10. A copolymer as claimed in any preceding claim having a molecular weight of 7000-13000.
11. A copolymer as claimed in any preceding claim wherein the molecular weight distribution (M_w/M_n) is 1.2-20.
- 5 12. A complex of a copolymer as claimed in any of claims 3 to 11, with a carboxylic acid.
13. A complex of a copolymer as claimed in any of claims 4 to 11, with a nitrogenous base.
- 10 14. A middle distillate oil comprising, as an additive, at least one copolymer as claimed in any of claims 1 to 11.
15. A middle distillate oil as claimed in claim 14, which is selected from the group consisting of kerosene, jet fuel, diesel fuel, heating oil, visbroken gas oil, light cycle oil, vacuum gas oil, light fuel oil and fuel oil.
- 15 16. A middle distillate oil as claimed in claim 14 or 15, which is in the form of a water in oil emulsion comprising 5-30% wt water.
17. A middle distillate oil as claimed in any one of claims 14 to 16, which contains at least one further additive, said further additive being selected from the group consisting of: a) a flow improver additive, (b) detergent, (c) anti foam, (d) ignition improver, (e) lubricity additive and (f) corrosion inhibitor.
- 20 18. Use of a copolymer as claimed in any one of claims 1 to 11 for reducing the wax deposition in a middle distillate oil.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/01495

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F8/12 C08F8/14 C08F8/30 C08F8/44 C10L1/22
C10M149/06 C10M149/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C10L C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

14 September 1999

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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